

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Highly efficient Mo₂C nanotube as a counter electrode catalyst for organic redox shuttle in dye-sensitized solar cell

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012Mingxing Wu,^{*a} Ya-nan Lin,^a Hongyue Guo,^a Kezhong Wu,^{*a} and Xiao Lin,^{*b}

DOI: 10.1039/x0xx00000x

www.rsc.org/

Molybdenum carbide nanotube (Mo₂C-NT) was synthesized which showed remarkable catalytic activity for regeneration of the organic sulfide redox shuttle. The dye-sensitized solar cell (DSC) using Mo₂C-NT as counter electrode (CE) showed a high power conversion efficiency of 6.22%, much higher than the DSC using conventional Pt CE (3.91%).

Dye-sensitized solar cell (DSC) received increasing attention due to the specific strengths of simple fabrication procedures, environmental friendliness, transparency, good plasticity, and ease of building combination.¹⁻³ In addition to the key components of the semiconductor and dye, the other two components of counter electrode (CE) catalyst and redox shuttle have also made great advancements.⁴⁻⁶ In DSC system, the CE functions as a catalyst, being responding for the regeneration of the redox shuttle. Therefore CE and redox shuttle relate to each other closely. Pt deposited on conductive fluorine-doped tin oxide (FTO) glass is commonly used as an effective CE.⁷ However the limited availability and high cost of Pt restricted its application in industrialization. I⁻/I₃⁻ is the widely used redox shuttle while this redox shuttle has the disadvantages of absorption of short-wave light and strong corrosion, which is a potential adverse factor for long-term use.⁸

Given the disadvantages of the Pt CE and I⁻/I₃⁻ redox shuttle, explore low-cost and Pt-free catalysts and iodide-free redox shuttles has become a hot research topic in DSC. It has been established that early transition metal carbides (TMCs) showed Pt-like behavior.⁹ In recent, we applied economical molybdenum carbide as the CE in I⁻/I₃⁻ electrolyte based DSC which produced a power conversion efficiency (PCE) of 5.83%, lower than the Pt CE based DSC (7.50%).¹⁰ For the redox shuttles, several iodide-free redox shuttles have been developed for DSC to replace the defective I⁻/I₃⁻, such as the organic sulfide redox shuttle of 5-mercapto-1-methyltetrazole N-tetramethylammonium salt /di-5-(1-methyltetrazole) (disulfide denoted as T⁻/T₂ for short) and the

T⁻/T₂ based electrolyte owns the merits of transparency and low viscosity.¹¹ Interestingly, we and other group found that Pt was not suitable for the regeneration of T⁻/T₂ redox shuttle.¹²⁻¹⁵ Thus it is urgent to develop new CE catalysts for the new redox shuttles. In this work, Mo₂C particle (Mo₂C-P) and Mo₂C nanotube (Mo₂C-NT) were synthesized for the T⁻/T₂ redox shuttle for the first time. As a result, the prepared Mo₂C, Mo₂C-NT in special, showed remarkable catalytic activity for T⁻/T₂ regeneration, far surpassing the expensive Pt.

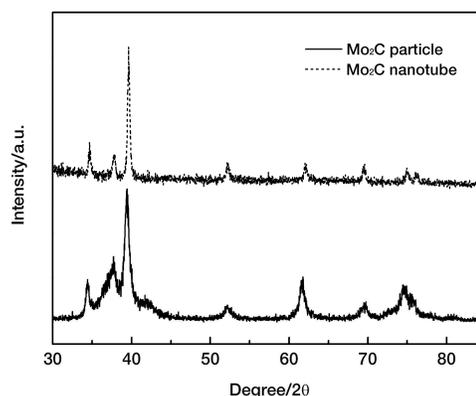


Fig. 1 XRD patterns of the prepared Mo₂C particle (Mo₂C-P) and Mo₂C nanotube (Mo₂C-NT).

First, Mo₂C-P was synthesized via urea glass route with MoCl₅ worked as metal source and urea as carbon source.¹⁶ In brief, proper amount of MoCl₅ was added to absolute ethanol to form Mo-orthoester. Then, a mount of urea were added to the Mo-orthoester to form urea-metal precursors. After removing the residual ethanol solvent and sintering the urea-metal precursor, Mo₂C-P was achieved. For achieving Mo₂C-NT, (NH₄)₆Mo₇O₂₄·4H₂O was used as metal source and phenylamine as carbon source. In this experiment, pH value should be controlled at 4~5 strictly to achieve the wirelike precursor (Fig.

S1). After sintering the precursor, Mo₂C-NT was collected. The XRD patterns in Fig. 1 indicated that Mo₂C-P and Mo₂C-NT were synthesized successfully (No. 11-0680, PDF-2 Database). For the Mo₂C-NT synthesized under 750 °C, the diffraction peak showed a low intensity, implying a weak crystallinity. In contrast, improve the sinter temperature from 750 to 1000 °C, Mo₂C-NT with high crystallinity was obtained (Fig. S2).

Fig 2 gives the morphologies of the prepared Mo₂C-P and Mo₂C-NT. Mo₂C-P interacted strongly and showed a worm-like appearance with an average size of 20~50 nm. In Fig. 2b and Fig. 3S, the SEM images showed the Mo₂C exhibited a typical nanotube profile with a mesoporous structure. A slight aggregation was observed as evidenced by the TEM image (Fig. 2c). The diameter of the Mo₂C-NT synthesized at 750 °C was around 25 nm (Fig. 2d). At a high sinter temperature of 1000 °C, a number of Mo₂C-NT adhered to each other and formed a thick Mo₂C-NT. The diameter was increased to 350~500 nm (Fig. 4S). The BET surface area of Mo₂C-P and Mo₂C-NT were 18.31 and 43.70 m² g⁻¹. The XRD, SEM, and TEM confirmed that Mo₂C-P and Mo₂C-NT were synthesized successfully.

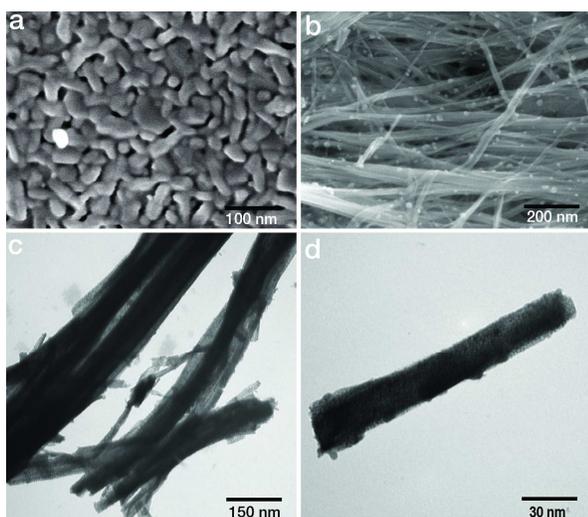


Fig. 2 SEM images of (a) Mo₂C-P and (b) Mo₂C-NT; TEM image of (c, d) Mo₂C-NT

As pointed out above, the Mo₂C-P has been used in I⁻/I₃⁻ electrolyte based DSC which generated a PCE of 5.83%, much lower than the Pt CE based DSC (7.50%).¹⁰ In this work, Mo₂C was applied in T⁻/T₂ electrolyte based DSC. Fig. 3a shows the current density-voltage (*J*-*V*) curves, and the photovoltaic parameters are summarized in Table S1. For T⁻/T₂ redox shuttle, the Mo₂C-P showed a high catalytic activity and the DSC gave a PCE of 5.50% (short-circuit current density, *J*_{sc}=13.66 mA cm⁻², open-circuit voltage, *V*_{oc}=636 mV, fill factor, FF=0.633). Most impressively, Mo₂C-NT behaved better than Mo₂C-P and the DSC using Mo₂C-NT CE yielded a higher PCE of 6.22% (*J*_{sc}=14.06 mA cm⁻², *V*_{oc}=637 mV, FF=0.694). In contrast, the DSC using Pt CE gave a low PCE of 3.91 (*J*_{sc}=13.05 mA cm⁻², *V*_{oc}=625 mV, FF=0.479). It can be clearly seen that *J*_{sc} and FF of the DSC using Mo₂C-NT CE are both higher than the corresponding parameters of the DSC based on Pt CE. This

shows the fact that the Mo₂C CE is more effective than Pt for the organic T⁻/T₂ redox shuttle, rather than the conventional I⁻/I₃⁻ redox shuttle.

To evaluate the catalytic properties of the as-prepared Mo₂C-P and Mo₂C-NT for the T⁻/T₂ redox shuttle, cyclic voltammetry (CV) was carried out in a three-electrode system. Fig. 3b depicts the cyclic voltammograms of the Pt, Mo₂C-P, and Mo₂C-NT electrodes. In the case of Pt, a typical pair of redox peaks were observed referring to redox reaction of T⁻/T₂.¹⁷ On one hand, the current densities of the reduction peak for Mo₂C-NT were much higher than Mo₂C-P and Pt. On the other hand, the oxydic and reductive potentials of the redox peaks of Pt were around -0.40 and 0.49 V, and the peak-peak separation ($\Delta E_{p, Pt}$) was 0.89 V. Compared with Pt, the cathodic peak for Mo₂C-NT shifted towards a more positive value (-0.22 V), whereas the anodic peak shifted towards a more negative value (0.29 V). Thus, the $\Delta E_{p, Mo_2C-NT}$ was only 0.51 V. According to the Nernst equation, the electrode can be recognized reversible for the T⁻/T₂ redox reaction. Moreover, ΔE_p varied inversely with *k*_s (charge transfer rate).¹⁸ Mo₂C-NT electrode showed a larger *k*_s value than Pt, which was constructive to the high catalytic activity. Similar to Mo₂C-NT, Mo₂C-P also provided a small ΔE_p value as well, indicating a good reversibility. Based on an overall consideration of the CV results, it was proved that Mo₂C-NT and Mo₂C-P are more effective than Pt for the regeneration of the T⁻/T₂ redox shuttle and Mo₂C-NT performed the best.

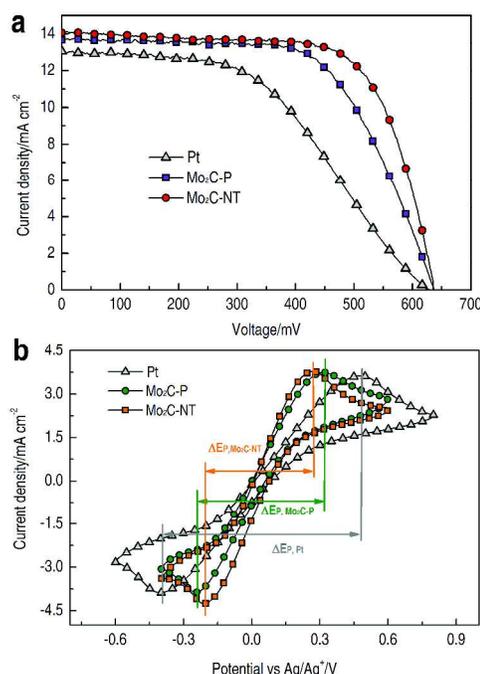


Fig. 3 current density-voltage (*J*-*V*) of the DSC using Pt, Mo₂C-P, and Mo₂C-NT counter electrodes.

Electrochemical impedance spectroscopy (EIS) is an effective tool to reveal the charge transfer process and further to evaluate the catalytic activity of a catalyst. Fig. 4a shows the Nyquist plots for the symmetrical cells fabricated with two identical electrodes. In the case of Pt, the intercept on the real

axis can generally be attributed to the series resistance (R_s). The left arch can be assigned to the charge transfer resistance (R_{ct}) and the corresponding capacitance (C_{μ}) of the electrode/electrolyte interface. The right arch can be assigned to the Nernst diffusion impedance (Z_N) of the T^-/T_2 redox shuttle in the electrolyte. The EIS data were obtained by fitting the Nyquist plots with an equivalent circuit diagram (inset in Fig. 4a), and the fit parameters are summarized in Table S1. No obvious difference of the R_s was found for the three electrodes. The R_{ct} values of Mo₂C-P and Mo₂C-NT were 2.0 and 0.8 Ω , much lower than the R_{ct} of Pt (8.1 Ω). This implies that Mo₂C has a high catalytic activity for T_2 reduction. In addition, Mo₂C-P and Mo₂C-NT showed low Z_N relative to Pt. And the Z_N of Mo₂C-NT was much lower than that of Mo₂C-P, stemming from the mesoporous structure of the Mo₂C-NT as shown in the TEM images. Both R_{ct} and Z_N demonstrated that the redox reaction between T^- and T_2 occurred easily on the Mo₂C-NT electrode, followed by Mo₂C-P and Pt electrodes. Moreover, Tafel polarization measurements were also applied to reconfirm the catalytic activity of the Mo₂C-P and Mo₂C-NT. Fig. 4b shows the Tafel curves for symmetrical cells similar to the ones used in the EIS measurements. The curves show logarithmic current density as a function of voltage and the details information of Tafel curve can be obtained in previous work.¹⁰ The curves of Mo₂C-P and Mo₂C-NT exhibited a large exchange current density (J_0) as compared to Pt electrode. This means that Mo₂C-P and Mo₂C-NT have superior catalytic activity for T_2 reduction which in good accordance with the EIS results. In theory, J_0 varies inversely with R_{ct} . With the EIS results, the change tendency of J_0 for various electrodes is generally in accordance with those presented in the Tafel curve plots. After performing a comprehensive analysis of the EIS and Tafel polarization curve results, we conclude that the Mo₂C is more suitable than Pt for T^-/T_2 redox shuttle and among the two kinds of Mo₂C compounds, the nanotube behaviours better undoubtedly.

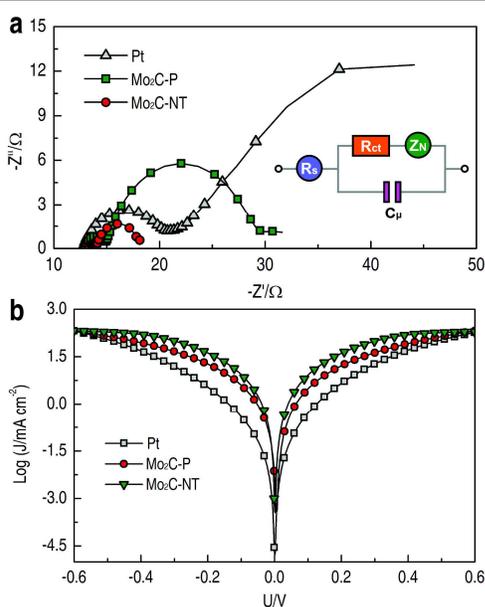


Fig. 4 (a) Nyquist plots and (b) Tafel curves of the symmetrical cells fabricated with Pt, Mo₂C-P, and Mo₂C-NT electrodes

Conclusions

In summary, combined with the T^-/T_2 electrolyte, Mo₂C nanotube was used as counter electrode catalyst in DSC system for the first time. The Mo₂C nanotube gave an impressive catalytic activity and the device yielded a high power conversion efficiency of 6.22%, a great enhancement of 59% as compared to the Pt CE based DSC (3.91%). The results reveal that Mo₂C nanotube is a promising alternative to the expensive Pt in DSC system.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Grant No. 21303039), Natural Science Foundation of Hebei Province (Grant No. B2013205171), Support Program for Hundred Excellent Innovation Talents from the Universities of Hebei Province, BR2-220), and Scientific Research Foundation for Introduction of Talents of Hebei Normal University.

Notes and references

^a College of Chemistry and Material Science, Key Laboratory of Inorganic Nano-materials of Hebei Province, Hebei Normal University, No. 20 Rd. East of 2nd Ring South, Yuhua District, Shijiazhuang City, Hebei Province, 050024, P. R. China. E-mail: mingxing@mail.ustc.edu.cn; Tel. & Fax: 86-311-80787438

^b Address here Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Jialuo Road 2019, Shanghai, 201800, P.R. China

Electronic Supplementary Information (ESI) available: [the details of preparing Mo₂C particle and nanotube and cell fabrication]. See DOI: 10.1039/c000000x/

- 1 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
- 2 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.
- 3 M.-E. Rifaoussi, M. Ince and T. Torres, *Eur. J. Org. Chem.*, 2013, 6475.
- 4 M. Wu and T. Ma, *ChemSusChem*, 2012, **5**, 1343.
- 5 M. Wang, C. Grätzel, S. M. Zakeeruddin and M. Grätzel, *Energy Environ. Sci.*, 2012, **5**, 9394.
- 6 H. Choi, C. Nahm, J. Kim, C. Kim, S. Kang, T. Hwang and B. Park, *Current Appl. Phys.*, 2013, **13**, S2.
- 7 Y. Wang, C. Zhao, D. Qin, M. Wu, W. Liu and T. Ma, *J. Mater. Chem.*, 2012, **22**, 22155.
- 8 E. Olsen, G. Hagen and S. E. Lindquist, *Sol. Energy Mater. Sol. Cells*, 2000, **63**, 267.
- 9 R. B. Levy and M. Boudart, *Science*, 1973, **181**, 547.
- 10 M. Wu, X. Lin, Y. Wang, L. Wang, W. Guo, D. Qi, X. Peng, A. Hagfeldt, M. Grätzel and T. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 3419–3428.
- 11 M. Wang, N. Chamberland, L. Breau, J.-E. Moser, R. Humphry-Baker, B. Marsan, S. M. Zakeeruddin and M. Grätzel, *Nat. Chem.*, 2010, **2**, 385.

- 12 H. Tian, Z. Xu, A. Hagfeldt, L. Kloo and L. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 9413.
- 13 M. Wu, X. Lin, L. Wang, Y. Wang, J. Xiao, A. Hagfeldt and T. Ma, *J. Phys. Chem. C*, 2011, **115**, 22598.
- 14 S. Pan, Z. Yang, H. Li, L. Qiu, H. Sun and H. Peng, *J. Am. Chem. Soc.*, 2013, **135**, 10622.
- 15 M. Wu, Y. Wang, X. Lin, N. Yu, L. Wang, L. L. Wang, A. Hagfeldt and T. Ma, *Phys. Chem. Chem. Phys.*, 2011, **13**, 19298.
- 16 C. Giordano, C. Erpen W. Yao and M. Antonietti, *Nano Lett.*, 2008, **8**, 4659.
- 17 M. Wu, B. Jin, Y. Wang, A. Wang, X. Lin, L. Wang, Y. Shen, Z. Wang, A. Hagfeldt and T. Ma, *J. Mater. Chem.*, 2012, **22**, 11121.
- 18 R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351.